

CPP 24: Glasses and Glass Transition I (jointly with DY and DF)

Time: Wednesday 14:00–17:30

Location: H48

Invited Talk

CPP 24.1 Wed 14:00 H48

New Approach to the Old Problem: Cooperativity in Dynamics of Glass Forming Systems — ●ALEXEI SOKOLOV — Oak Ridge National Lab and UT Knoxville, USA

The mechanism behind the steep slowing down of molecular motions upon approaching the glass transition remains a great puzzle. Most of the theories relate this mechanism to the cooperativity in molecular motion. In this talk we present estimates and analysis of the molecular cooperativity in many glass-forming systems. We demonstrate that the cooperativity length scale directly correlates to the dependence of the structural relaxation on volume. This dependence presents only one part of the mechanism of slowing down the structural relaxation. Our analysis reveals that another part, the purely thermal variation of the structural relaxation, does not have a direct correlation with molecular cooperativity. These results call for a conceptually new approach to the analysis of the mechanism of the glass transition and to the role of molecular cooperativity in slowing down of structural relaxation.

CPP 24.2 Wed 14:30 H48

THz Signatures of the Glass Transitions in Polymers — ●MARCO REUTER¹, STEFFEN WIETZKE^{2,3}, CHRISTIAN JANSEN^{2,3}, TILMANN JUNG¹, SANGAM CHATTERJEE¹, WIEBKE DEMPWOLF⁴, HENNING MENZEL⁴, and KOCH MARTIN^{1,3} — ¹Fachbereich Physik, Philipps-Universität Marburg, Renthof 5, 35032 Marburg, Germany — ²Institut für Hochfrequenztechnik, TU Braunschweig, Schleinitzstr. 22, 38106 Braunschweig, Germany — ³Joint Optical Metrology Center, c/o TU Braunschweig, Fakultät für Elektrotechnik und Informationstechnik, Hans-Sommer-Str. 66, 38106 Braunschweig, Germany — ⁴Institut für Technische Chemie, TU Braunschweig, Hans-Sommer-Str. 10, 38106 Braunschweig, Germany

The glass transition temperature of polymers is found with terahertz time-domain spectroscopy. In the region of the glass transition the thermo-quasi-optic coefficient changes noticeably. THz time-domain spectroscopy is a non-destructive and non-contact technique to analyse polymers.

CPP 24.3 Wed 14:45 H48

The elusive nature of the Debye process in monohydroxy alcohols: A new approach with ²H-NMR techniques — ●SEBASTIAN SCHILDMANN, CATALIN GAINARU, and ROLAND BÖHMER — Experimentelle Physik III, Fakultät für Physik, Technische Universität Dortmund

Viscous monohydroxy alcohols, also water, exhibit a so called Debye process in their dielectric spectra. This relaxational feature corresponds to degrees of freedom which are about 100 times slower than those giving rise to the structural rearrangements (α -process). In spite of numerous experimental investigations [1], the nature of these slow "superstructure" relaxation modes is not agreed upon, although it is clear that they are to be related with the presence of hydrogen bonds. The Debye process separates from the structural process if the network is interrupted chemically by diluting or topologically by confining the system in pores. Here butanol diluted with bromobutane was studied with several ²H-NMR techniques. Correlation times measured with stimulated-echo experiments are compared with data obtained from dielectric spectroscopy [2]. Spin-lattice relaxation times were measured for O-D deuterated samples to check how the hydrogen bonds affect the dynamics.

[1] M. Poeschl & H.G. Hertz, *J. Phys. Chem.* 98, 8195 (1994).

[2] T. El Goresy & R. Böhmer, *J. Chem. Phys.* 128, 154520 (2008).

CPP 24.4 Wed 15:00 H48

Relaxation Kinetics of Nanoscale Indents in a Polymer Glass — ●ARMIN KNOLL, DOROTHEA WIESMANN, BERND GOTSMANN, and URS DUERIG — IBM Research - Zurich, 8803 Rüschlikon, Switzerland
Nanometer scale indents have been written in a cross-linked polystyrene sample, and their relaxation has been studied at annealing temperatures well below the glass transition of the polymer. The indents represent a highly nonequilibrium state of the polymer which is subjected to mechanical stress of up to 0.4 GPa and thermal quench rates on the order of 10⁸ K/s during writing. It is shown that the relaxation towards equilibrium evolves logarithmically over more than 10 orders of magnitude in time. The relaxation kinetics are accurately de-

scribed in terms of a thermally activated process with an energy barrier whose magnitude decreases linearly with the distance from equilibrium [1].

[1] A. Knoll, D. Wiesmann, B. Gotsmann, and U. Duerig, *Phys. Rev. Lett.*, **102**, 117801 (2009)

CPP 24.5 Wed 15:15 H48

Studying the dynamics of water molecules on a complex lattice: KOH doped tetrahydrofuran clathrate hydrate — ●HELGE NELSON¹, CATALIN GAINARU¹, ANDRE NOWACZYK¹, SEBASTIAN SCHILDMANN¹, BURKHARD GEIL², and ROLAND BÖHMER¹ — ¹Experimentelle Physik III, Fakultät für Physik, TU Dortmund — ²Institut für Physikalische Chemie, Universität Göttingen

Because of kinetic hindrance during the freeze-out of the protons in clathrate hydrates an orientational glass transition is observed. By adding minute amounts of ionic dopants, e.g., KOH, the timescale of ordering can be accelerated significantly and an ordered phase is reached [1]. We applied a combination of dielectric and ²H-NMR techniques to study the lattice dynamics of the water molecules in a temperature range from 30 K to 260 K. The ²H-NMR techniques include temperature dependent lineshape analysis, measurement of relaxation times, and the stimulated-echo technique. This combination allows the observation of dynamics in a broad frequency and temperature window. We found several reorientational processes on the lattice, which are absent in the undoped sample. In addition we were able to detect the phase transition into the proton ordered phase with both dielectric and NMR measurements close to 62 K.

[1] see O. Yamamuro, et al., *Physica B* 213, 405 (1995) and references cited therein.

15 min. break**Invited Talk**

CPP 24.6 Wed 15:45 H48

Slow domains percolation in polymer melts and blends close to the glass transition: a unifying concept regarding bulk dynamics, dynamics in the vicinity of interfaces, and the physical properties of nanocomposites — ●DIDIER R. LONG — Laboratoire Polymères et Matériaux Avancés; CNRS/Rhodia; F-69192 Saint Fons, France.

Experiments have demonstrated over past 15 years that the dynamics in liquids close to and below the glass transition temperature is strongly heterogeneous, on the scale of a few nanometers and, independently, that the glass transition temperature in the vicinity of interfaces can be very different from that in the bulk, with shifts either positive or negative depending on the interaction between the polymer and the interface. By considering thermally induced density fluctuations in the bulk, we proposed that the 3-D glass transition is controlled by the percolation of small domains of slow dynamics, which allows to explain the heterogeneous dynamics close to T_g. This model allowed then for interpreting a priori unrelated features of polymer dynamics: 1) the main feature of confinement effects on the dynamics; 2) Unique reinforcement, plastic and recovery behaviour of nano-filled elastomers; 3) ageing and rejuvenating dynamics polymeric liquids; 4) case II diffusion, which is how a solvent penetrates and finally melts a glassy polymer matrix.

Regarding these various issues, I will put the emphasis on how percolation of slow domains is key for explaining their main features.

CPP 24.7 Wed 16:15 H48

Glass Transition of Molecules Sorbed in Zeolites — ÖZLEN F. ERDEM¹, ●DIETER MICHEL², PAVEL SEDYKH², and JÜRGEN HAASE² — ¹Max-Planck-Institute of Bioinorganic Chemistry, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany — ²University of Leipzig, Faculty of Physics and Earth Sciences, Linnéstraße 5, 04103 Leipzig, Germany

Proton MAS NMR, nuclear spin relaxation, and deuteron NMR spectroscopy are combined to study the mobility of ethylene glycol molecules sorbed in various zeolites over a wide temperature range. The results obtained will be also compared with broad-band dielectric measurements and with previous extensive dielectric studies by Kremer *et al.* [1]. The main question is whether the adsorbed species show a so called single-molecule behavior characterized by an Arrhenius

type temperature dependence of the correlation times or the respective dielectric relaxation times. In contrast, a Vogel-Fulcher-Tammann (VFT) type temperature dependence of the dielectric relaxation rate would point out collective motions and is typical for the appearance of a glass-transition. An important question is the competition between molecule-to-molecule and molecule-to-surface interactions.

[1] F. Kremer, A. Huwe, M. Arndt, P. Behrens, W. Schwieger, J. Phys. Cond. Mat. **11**, A175-A188 (1999); A. Huwe, F. Kremer, J. Kärger, P. Behrens, W. Schwieger, G. Ihlein, O. Weiss, F. Schuth, J. Mol. Liquids **86**, 173-182 (2000).

CPP 24.8 Wed 16:30 H48

Molecular glass formers in hard and soft confinement probed by ^{31}P and ^2H NMR — •DANIEL BOCK, SABINE GRADMANN, and ERNST RÖSSLER — Experimentalphysik II, Universität Bayreuth

Low molecular glass formers confined in nanoporous silica matrices (hard confinement) are investigated by different ^{31}P and ^2H NMR methods such as spin-lattice-, spin-spin relaxation, line-shape and stimulated echo decay.

Decreasing the radius of the pores pronounced dynamic heterogeneities are observed. For example, the correlation function revealed by the stimulated echo exhibits a quasi-logarithmic decay in contrast to Kohlrausch decay in the bulk. As shown by 2D spectra the dynamic heterogeneities are transient in time, i.e., we observe exchange between slow and fast molecules. The effects are explained by assuming dynamics being inhomogeneous in space; that is the dynamics given by a correlation time $\tau(r)$ depend on the distance r from the confining wall.

Similar NMR features are found for low molecular additives dissolved in polymer matrices (soft confinement). The additive dynamics are decoupled from those of the polymer, and liquid-like additive dynamics are revealed below T_g , i.e., in a solid polymer matrix. Again, strongly stretched correlation functions are observed.

CPP 24.9 Wed 16:45 H48

Quantitative Lineshape Analysis for 1D- and 2D-Spectra of Amorphous Materials — •JÖRN SCHMEDT AUF DER GÜNNE, SABARINATHAN VENKATACHALAM, JOHANNES WEBER, and YAMINI AVADHUT — Department of Chemistry, Munich University (LMU), Germany

NMR is quantitative, is an often stated feature in magnetic resonance. In ^1H solid-state NMR the results from simple MAS experiments can be disappointing though. We present a model study [1] which identifies and quantifies different sources of errors and a new strategy which gives reliable results even under low resolution conditions.

A second aspect will be 2D deconvolution of the lineshapes of amorphous/glassy materials. We analyze the unexpected splittings in the 2D lineshape of many typical glasses with a new analytical fitting function. Based on these findings we suggest a structural model based on different subunits, which should also find their imprint in bulk properties.

[1] Y.S.Avadhut, D.Schneider, J.Schmedt auf der Günne, J. Magn. Reson. **201** (2009) 1-6.

CPP 24.10 Wed 17:00 H48

Low-Frequency Excess Contribution in Simple Liquids Revealed by Fast Field Cycling NMR — •ROMAN MEIER, AXEL HERRMANN, ROBERT KAHLAU, DANUTA KRUK, and ERNST RÖSSLER — Experimentalphysik II, Universität Bayreuth, Germany

The main relaxation (α -relaxation) of simple liquids studied by dielectric spectroscopy is well described by a Cole-Davidson (CD) susceptibility. In particular the low-frequency limit follows a Debye behavior $\chi''_{DS} \propto \omega^{-1}$. Applying fast field cycling (FFC) ^1H NMR and transforming the spin-lattice dispersion data T_1 into the susceptibility representation $\chi''_{NMR} \propto \nu/T_1$ we have discovered a low-frequency excess contribution for systems like glycerol and its homologues as well as fluoroaniline. The CD function fails to describe the data due to a retarded transition to the limit ω^{-1} , i.e., a “shoulder” is observed on the low frequency side of the α -relaxation peak ($\omega\tau_\alpha < 1$) possibly reflecting a slower relaxation process. Actually only a few liquids like o-terphenyl and tristyrene studied by FFC NMR do not show this phenomenon. Collecting dispersion data over a large temperature range, the relaxation strength of the excess contribution is specified quantitatively. Measurements of dilution series of propylene glycol in deuterated chloroform proved an intermolecular origin of the excess contribution. Dilution experiments of deuterated in protonated glycerol suggest this additional contribution being also fully reflected by sole intramolecular spin-spin vectors. A possible explanation of this effect are transient molecular clusters due to chemical interactions (e.g. H-bonds).

CPP 24.11 Wed 17:15 H48

Glass transition of colloidal particles with long-ranged interactions in two dimensions — •DAVID HAJNAL, MARTIN OETTEL, and ROLF SCHILLING — Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, D-55099 Mainz, Germany

We study the glass transition behavior of binary mixtures of colloidal particles with long-ranged dipolar interactions in two dimensions in the framework of mode-coupling theory (MCT). We first present a minimal model for the theoretical description of the thermodynamic properties of the experimental system studied by König et al. [1]. By applying MCT to this model, we determine its glass transition diagram, i.e. we calculate the variation of the critical interaction strength upon composition changes. Finally, we compare the mixing effects predicted by MCT for this model to both experiments [1] and MCT results for binary mixtures of hard disks [2].

[1] H. König, R. Hund, K. Zahn, and G. Maret, Eur. Phys. J. E **18**, 287 (2005).

[2] D. Hajnal, J. M. Brader, and R. Schilling, Phys. Rev. E **80**, 021503 (2009).